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Electronic structure, carrier mobility and device properties for mixed-edge phagraphene nanoribbon by hetero-atom doping

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ABSTRACT

Phagraphene, a new carbon allotrope, was proposed recently. We here select a mixed-edge phagraphene ribbon to study B-, N-, and BN-doping effects respectively on the geometric stability, electronic structure, carrier mobility, and device property. Calculations show that the energetic and thermal stability for these ribbons are very high. With different doping types and doping sites, the bandgap size of a ribbon may be nearly unchanged, increased, or decreased as compared with the intrinsic ribbon, and even become a metal, thus presenting fully tunable electronic structures. For this, the charge transfer shifting edge bands and the new formed hybridized bands due to doping play a crucial role. More interestingly, doping at different positions can regulate the carrier mobility of ribbon, and the difference of two orders of magnitude for hole mobility can be generated by BN-doping. In addition, the study on device property shows that there is a prominent negative differential resistance characteristics occurring in a BN-doped ribbon device. These findings are meaningful for understanding the doping effects on electronic properties of phagraphene nanoribbons.

1. Introduction

Graphene, one of the most extensively studied two-dimensional (2D) materials in recent years, consists of carbon atoms by hexagonal symmetric lattice, resulting in its band structure like Dirac cones with linear dispersion near the Fermi level [1]. And graphene presents many novel properties, such as quantum Hall effect [2,3], ultrahigh thermal conductivity and super-flexibility [4]. In particular, its carrier mobility can reach 10^5 cm^2 V^{-1} s^{-1} orders of magnitude at room temperature [5]. This make it possible becoming a promising alternative for developing the next-generation high-performance functional devices. Meanwhile, the successful fabrication of graphene also encourage researchers to explore other 2D materials. So far, beyond graphene, numerous other 2D materials have also been proposed or fabricated, such as silicene [6], h-BN [7–9] and borophene [10], MoS2 [11], and phosphorene [12]. Especially for carbon-based 2D atomic crystals, such as graphane [13], graphdiyne [14,15], and penta-graphene [16,17], all of which demonstrate novel and exceptional electronic features.

Recently, a new carbon allotrope with a planer structure composed of 5-6-7 carbon rings, phagraphene, was predicted to be stable [18]. This 2D material made out of sp^2-hybrid carbon atoms possesses a high atomic packing density, allowing that its physical properties could be comparable with graphene and its geometrical structure is energetically more favorable than other carbon allotropes proposed previously [18,19]. Intrinsic phagraphene is a semimetal with the band structure like distorted Dirac cones near the Fermi level [19]. By using a molecular dynamics simulations, Pereira et al. [20]reported that the thermal conductivity of phagraphene is anisotropic, and the predicted electronic properties suggest that phagraphene could be a better candidate than graphene in future carbon-based thermoelectric devices. Unfortunately, the lack of band gap in phagraphene will be an obstacle for realistic applications in future electronic devices. Similar to graphene, the very simple and feasible strategy to solve this issue is cutting phagraphene sheet into quasi-one dimensional narrowed nanoribbons, phagraphene nanoribbons (PHAGNRs). The electronic properties of PHAGNRs would be ruled by atomic geometries along edges. For example, Liu et al. [21]reported that hydrogen-terminated PHAGNRs with mixture of armchair and zigzag shaped edges are semiconducting, and hydrogen-terminated pure zigzag PHAGNRs behave as a metal.

In previous works, in order to tune functional properties of

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graphene or derived graphene nanoribbons adequately for realizing applications in more fields, one of the usually used routines is doping them with foreign atoms [22–30] or to constitute the hetero-structure [31–34]. Among these doping schemes, B or/and N atom doping is more preferred. This is because the chemical properties of N and B atoms are similar to C atoms, and thus forming a quite strong covalent B (N)-C bond, similar to the C–C bond. The geometric deformation for graphene induced by the N or/and B doping is also very small. They modulate electronic properties of graphene only by introducing extra carries and changing energy band structures, therefore, the N or B atom or BN molecule doping has become typical substitutional doping in graphene. So far, B- or/and N-doped graphene have been synthesized in many experiments [28–30,35,36], including a large area h-BNC film being fabricated, which presents different physical properties from h-BN film and graphene sheet [36]. Particularly, with the continuous enhancement of the experimental technology, for example, single carbon atom can be knocked off by focused electron beam of 1 Å diameter [37], and an atomic force microscope (AFM)has been applied to achieve various single-atom manipulations [38], the atom-doping trends to be more ordered, and even to be feasible to realize site-selective substitutional doping with atomic precision [39]. However, there are no reports about doping for phagraphene to modulate electronic properties until now, including B or/and N doping.

In this present work, based on the first-principles method, we study the geometrical stability, electronic structure, carrier mobility, and device property for a mixed-edge phagraphene ribbon with B-, N-, and BN- doping, respectively. Calculations show that the energetic and thermal stability for these ribbons is very high, and they hold diverse electronic structures upon the dopant types and doping sites. For this, the charge transfer moving edge bands and new formed hybridized bands due to doping play a crucial role. In particular, doping can regulate the carrier mobility of ribbons, and the difference of two orders of magnitude for hole mobility can be generated by BN-doping. In addition, constructed devices based on these ribbons exhibit there is a prominent negative differential resistance characteristics occurring in a BN-doped ribbon device.

2. Structure Models and Theoretical Method

The schematic diagram for the atomic structure of 2D phagraphene is demonstrated in Fig. 1(a), and when tailoring it along x direction, we can obtain one kind of typical nanoribbon, MPHAGNR, whose each edge is a mixture structure of alternating armchair and zigzag segments. A MPHAGNR contains two classes of carbon chains across its width direction, both pure zigzag-type carbon chains and mixture-type carbon chains consisting of alternating armchair and zigzag segments. Thus, the width of a MPHAGNR, W, is defined as the total number of two classes of carbon chains. Here, we choose a ribbon with W = 6 as representative. To eliminate the emerging dangling bonds at ribbon edges due to tailoring phagraphene, all the ribbon models are saturated with single hydrogen atoms at both edges. Fig. 1(b) shows a unit cell, which represents a smallest repeatable unit of the periodical structure along the length direction of ribbon, denoted by a red dotted box. We select such a unit cell for calculation. To functionalize MPHAGNRs, we consider a substitutional doping with B or/and N. Of course, doping schemes may be diverse. To lower the complexity, we take into account B or/and N substitutional doping only occurring in one pentagon carbon ring per unit cell, highlighted by a crimson-filled area in Fig. 1(b). However, when only one B or N atom is doped into such a pentagon carbon ring. Our calculations exhibit that its influence on the electronic structures is very small due to a too lower doping concentration. Accordingly, single B-B or N-N doping (dopant unit) in a pentagon carbon ring is, respectively, implemented in our study besides B-N doping, as shown in Fig. 1 (c)-(e), respectively, where gray balls represent C atoms, white balls H atoms, pink balls B atoms, and blue balls represent N atoms. Meanwhile, such three kinds of doping manners also make it possible for the calculated results to be compared with each other due to the same doping concentration and coverage fraction. In addition, our calculation also suggests that there is not a significant impact on structural stability for B-B (N-N) doping as compared with one B (N) atom doping. The doping positions marked as P1, P2, P3, P4, and P5, respectively, as shown in Fig. 1 (c)-(e) as well. Owing to structural symmetry, the results of B-B or N-N doping at positions P1 and P3, as well as P4 and P5, are exactly the same. Therefore, we only put B-B (N-N) doping at positions P1, P2, and P4 into investigations. For simplicity, the B-B, N-N, and B-N doping are hereafter called as the B-, N-, and BN- doping, respectively.

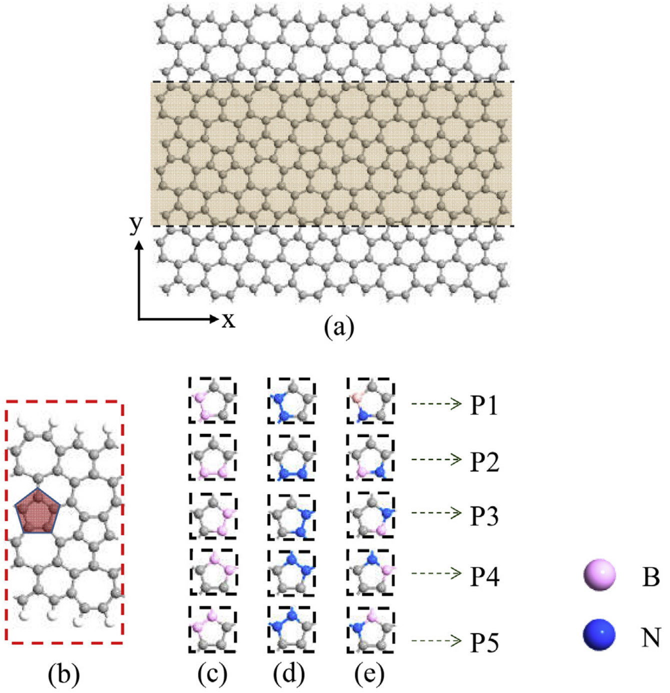

Fig. 1. (a) Schematic of 2D phagraphene sheet, the shallow yellow area indicates a MPHAGNR tailored from the sheet along x direction. (b) A unit cell of MPHAGNR, the doping only occurs in a pentagon highlighted by a crimson-filled area. (c) B-B doping. (d) N-N doping, (e) B-N doping. Pi (i = 1,2 …,5) represents doping positions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The geometrical relaxations and calculations for electronic structure and transport properties for above all models are performed by the density functional theory (DFT) combined with the non-equilibrium Green's function (NEGF) technique as implemented in the Atomistix ToolKit (ATK) [40–44]. In order to solve the Kohn–Sham equation, The Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) is used as the exchange–correlation functional. Considering the polarized effects of atoms, the double-zeta plus polarization (DZP) basis set is used for all atoms. We employ Troullier–Martins norm-conserving pseudopotentials to represent the atom core and linear combinations of local orbitals to expand the valence states of electrons. In the Brillouin zone, the k-point sampling is chosen as 1 × 1 × 150, and 300 Ry is set as the cut-off energy for the grid integration, mainly controlling the size of the real space integral